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(54) Preparation of 1,1,1,3-tetrafluoropropene(1234ze)

(57) Disclosed is a process for the preparation of cis/trans 1,1,1,3-tetrafluoro-2-propene (1234 ze) which comprises (a) contacting 1,1,1,3,3-pentafluoropropane (245fa) with an alkaline solution, preferably an aqueous or alcoholic solution of a base such as KOH, NaOH, Ca $(OH)_2$ or $Mg(OH)_2$, or with a chromium-based catalyst, such as fluorided Cr_2O_3 or fluorided Cr/Ni/AlF_3, and (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the reaction mixture.

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Description

[0001] This invention relates to preparation of cis/trans 1,1,1,3-tetrafluoropropene ("1234ze"), a monomer useful for the preparation of various homopolymers and copolymers, particularly to processes for the dehydrofluorination of 1,1,1,3,3-pentafluoropropane ("245fa"), a known blowing agent, to 1234ze using a chromium-based catalyst or a strong base. While the prior art, R. N. Haszeldine, J. Chem. Soc., 1952 (3490), describes the synthesis of cis/trans 1,1,1,3-tetrafluoropropene by fluorination of 1,1,1-trifluoro-2-propyne, this latter feed stock material is not available commercially.

[0002] Herein provided is a process for the preparation of 1234ze which comprises

(a) contacting 245fa with an alkaline solution or with a chromium-based catalyst, and
(b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.

[0003] It has now been discovered that the cis and trans isomers of 1,1,1,3-tetrafluoro-2-propene (1234ze) can be conveniently prepared by dehydrofluorination of the blowing agent, 245fa, using either a strong base (either an aqueous or alcoholic solution) or a chromium-based catalyst.

[0004] The catalyzed process is preferably carried out in the gas phase. Use of an oxygen-containing gas such as air is desired to extend the catalyst lifetime, the level of oxygen generally being from about 1 to about 10 volume percent (preferably about 2 to 5%), based on the volume of the organic feed. Temperatures of from about 100°C. to about 600°C. are typically used, preferably from about 300°C. to about 400°C. The pressure can be atmospheric. Contact time (total flow rate per catalyst volume) is typically from about 1 to about 60 seconds, preferably from about 20 to 50 seconds. The catalyst is a chromium-based catalyst such as fluorided chromium oxide, Cr_2O_3, which chromium-based catalyst is either unsupported or supported on a support such as activated carbon, graphite, fluorided graphite or fluorided alumina, the chromium catalyst being used alone or in the presence of a co-catalyst selected from a nickel, cobalt, manganese or zinc salt. Two such preferred chromium catalysts are high surface area chromium oxide and chromiuminickel on fluorided alumina ($Cr/Ni/AlF_3$), preparation of this latter catalyst being taught, for example, in European Patent 486333. The chromium-based catalysts are preferably activated before use, typically by a procedure wherein the catalyst bed is heated to about 370°-380°C. (normally with a continuous flow of nitrogen), after which a mixture of approximately equal volumes of HF and air or nitrogen (preferably nitrogen) are fed over the catalyst bed for about 18 hours.

[0005] The dehydrofluorination can also be accomplished using an alkaline solution of a strong base, such as an aqueous or alcoholic solution of potassium hydroxide (KOH), sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$) or magnesium hydroxide ($Mg(OH)_2$). For the alcoholic solution, a conventional alcohol such as ethanol can be used. The solution typically is from about 0.01 to about 10 molar, preferably 0.1 to 5 molar. The dehydrofluorination is typically conducted at a temperature of from about 20°C. to about 100°C., preferably from about 20°C. to about 50°C.

[0006] The following examples are illustrative.

[0007] Example 1. 52.4 Grams of a high surface area Cr_2O_3 catalyst was activated by first feeding 30 ccm of nitrogen for 2 hours at 370°C. followed by cofeeding 30 ccm of HF and 30 ccm of nitrogen for 18 hours at 370°C. Subsequently, a mixture of 20 ccm of 245fa and 3 ccm of air (equal to about 3 volume % of oxygen, based on the 245fa volume) was fed over the catalyst bed at 400°C for a contact time of 45 seconds. Conversion was 96.2%. Selectivity for the desired (1234ze) product was about 96.3% (about 18.5% cis, about 77.8% trans). Performance of the catalyst was steady for 360 hours.

[0008] Example 2. Example 1 was repeated using $Cr/Ni/AlF_3$ catalyst (activated at 370°C. using a cofeed of 30 ccm of nitrogen and 30 ccm of HF for 18 hours) in a series of 3 tests, using the same temperature and air/245fa feed ratio, but with the contact time between 26 and 39 seconds. Conversions ranged from 88 to 94.5%. Selectivity for the desired (1234ze) product ranged from 96.2 to 98.5% (17.7 to 20.5% cis, 77 to 80.5% trans).

[0009] Example 3. 10 ccm of 245fa was bubbled through 3000 ml of 2.7 molar KOH solution at room temperature (about 20°C.). Analysis of the gaseous dry product, using gas chromatography on line, showed 26% conversion, with selectivity for the desired (1234ze) product of 97.9% (23.9% cis, 74% trans).

Claims

1. A process for the preparation of cis/trans 1,1,1,3-tetrafluoro-2-propene which comprises (a) contacting 1,1,1,3,3-pentafluoropropane with an alkaline solution or with a chromium-based catalyst, and (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.

2. A process for the preparation of cis/trans 1,1,1,3-tetrafluoro-2-propene which comprises (a) contacting 1,1,1,3,3-pentafluoropropane with an aqueous or alcoholic solution of base selected from the group consisting of potassium hydroxide, sodium hydroxide, calcium hydroxide or magnesium hydroxide, and (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.

3. A process as in Claim 2 wherein step (a) comprises contacting 1,1,1,3,3-pentafluoropropane with an aqueous potassium hydroxide solution.

4. A process for the preparation of cis/trans 1,1,1,3-tetrafluoro-2-propene which comprises (a) contacting 1,1,1,3,3-pentafluoropropane with an oxygen-containing gas in the presence of a fluorided catalyst selected from Cr_2O_3 or $Cr/Ni/AlF_3$, and (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.

5. A process as in Claim 4 wherein the catalyst is fluorided Cr_2O_3.

6. A process as in Claim 4 wherein the catalyst is fluorided $Cr/Ni/AlF_3$.

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EUROPEAN SEARCH REPORT

Application Number
EP 99 30 5781

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	KNUNYANTS I L ET AL: "REACTIONS OF FLUORO OLEFINS. COMMUNICATION 13. CATALYTIC HYDROGENATION OF PERFLUORO OLEFINS" BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR, DIVISION OF CHEMICAL SCIENCES, 1 January 1960 (1960-01-01), pages 1312-1317, XP000578879 ISSN: 0568-5230 See p. 1313, reaction (XI) -> (XIII) and p. 1316, sixth paragraph. ---	1-3	C07C17/25
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	15 February 2000	Janus, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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DOCUMENTS CONSIDERED TO BE RELEVANT

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The present search report has been drawn up for all claims

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MUNICH	15 February 2000	Janus, S

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 99 30 5781

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